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(54) Title: LOW MOISTURE LAUNDRY DETERGENT BAR WITH IMPROVED PHYSICAL PROPERTIES

(57) Abstract

The present ivention relates to LAS and bleach containing laundry bar compositions comprising a low moisture content of no more than about 3.5 % in the finished product composition and the addition of an effective amount of divalent metal sulfates, which delivers significant improvement in bar physical properties.

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LOW MOISTURE LAUNDRY DETERGENT BAR WITH IMPROVED PHYSICAL PROPERTIES

FIELD OF THE INVENTION

This invention relates to a laundry detergent bar composition having a low moisture content with improved physical properties. The process to make such compositions is also included herein.

BACKGROUND OF THE INVENTION

In societies where mechanical washing machines are not common, laundry detergent bars comprising synthetic organic surfactants and detergency builders are used in the laundering of clothes. Technical developments in the field of laundry detergent bars have concerned formulating bars which are effective in cleaning clothes; which have acceptable sudsing characteristics in warm and cool water and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Methods for making laundry detergent bars are also well known in the art. Prior art disclosing laundry bars and methods for making laundry bars include: U.S. Pat. 3,178,370, Okenfuss, issued April 13, 1965; and Philippine Pat. 13,778, Anderson, issued September 23, 1980.

A common anionic surfactant used in laundry bar compositions is linear alkyl benzene sulfonate (LAS). Bar compositions comprising high levels of LAS are soft and do not possess desirable physical properties. In addition, laundry bar compositions typically comprise moisture, wherein the presence of moisture also leads to bar softness.

Laundry compositions typically include bleach. The addition of bleach, especially peroxygen bleach, slightly improves the physical properties of bars containing high levels of LAS by hardening the bars, but is not sufficient to have acceptable physical properties; the bars are still too soft.

It has now been found that LAS containing bleach laundry bar compositions comprising a low moisture content of no more than about 3.5% in the finished product composition and the addition of an effective amount of divalent metal sulfates delivers significant improvement in bar physical properties.

SUMMARY OF THE INVENTION

The present invention relates to a laundry detergent bar composition comprising:

(a) from about 0.5% to about 60% synthetic anionic detergent surfactant, wherein at least 30% of the surfactant component is linear alkyl benzene sulfonate;

(b) from about 0.10% to about 60% bleach agent;

(c) no more than about 3.5% moisture in the finished bar composition; and

(d) from about 1% to about 20% divalent metal sulfates.

The amount of moisture is exclusive of water of hydration of the divalent metal sulfates if hydrated forms of the divalent metal sulfates are used.

All documents referenced herein are incorporated by reference.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims distinctly pointing out and particularly claiming that which is regarded as the invention, it is believed that the invention can be better understood through a careful reading of the following detailed description of the invention. In this specification all percentages are by weight, all temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point (.), unless otherwise indicated.

In accordance with the present invention it has been found that a laundry detergent bar can achieve bleach stability over time in a low moisture content bar composition.

Synthetic anionic detergent surfactants

Synthetic anionic detergent surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable

are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS. The alkali metal salts, particularly the sodium salts of these surfactants are preferred. Alkylbenzene sulfonates and processes for making them are disclosed in U.S. Patent Nos. 2,220,099 and 2,477,383.

Other synthetic anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates. Preparation of alkyl glyceryl ether sulfonates are described in detail in U.S. Pat. 3,024,273, Whyte et al., issued March 6, 1962.

In addition, suitable synthetic anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred anionic surfactants are C_{10-18} linear alkyl benzene sulfonates, C_{10-18} alkyl sulfates, and mixtures thereof.

The amount of synthetic anionic surfactant in the compositions herein is from about 0.5% to about 60%, preferably from about 10% to about 30%. Of the total amount of surfactant component, bars of the present invention comprise at least 30%, more preferably at least 50%, most preferably at least 70% linear alkyl benzene sulfonate.

Bleach Agent

The bleach agent in the detergent composition is preferably at a level from about 0.10% to about 60% by weight; more preferably, from about 1% to about 50%; most preferably, from about 1% to about 20%. The bleach agents used herein can be any of the bleach agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. Mixtures of bleach agents can also be used.

A useful bleach agent that can be used encompasses percarboxylic acid bleach agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleach

agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleach agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Other peroxygen bleach agents can also be used. Suitable peroxygen bleach compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

Bleach agents other than oxygen bleach agents are also known in the art and can be utilized herein. One type of non-oxygen bleach agent of particular interest includes photoactivated bleach agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

A useful percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

The preferred bleach agent for the present invention are those peroxygen bleaching compounds which are capable of yielding hydrogen peroxide in an aqueous solution. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used, if desired.

Preferred peroxygen bleaching compounds to be used in the present invention include sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particular preferred are sodium perborate

tetrahydrate, and especially, sodium perborate monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching solution.

Bar Physical Properties

The finished bar composition should have no more than about 3.5% moisture. Preferably, the bar will contain from about 0.5% to about 3.4% moisture, more preferably, 1.4% to 3%. The moisture level of the total finished bar composition can be determined by any method known in the art by one skilled in the area of laundry bar compositions. One common method is the Bidwell Sterling Distillation method. Another known method is the Karl Fischer Moisture Titration Method. See AOCS official method Dd2a-59 issue 93 and AOCS official method Dd2b-59 issue 89.

The limitation of no more than about 3.5% moisture in the finished bar composition of the present invention is exclusive of water of hydration from the divalent metal sulfates, if hydrated forms of divalent metal sulfates are used. The amount of moisture exclusive of water of hydration of the divalent metal sulfates can be determined as the difference between the total analyzed moisture in the finished bar composition and the known amount of water of hydration from the divalent metal sulfates.

Divalent Metal Sulfate

Although the bar has low moisture, it still has acceptable physical properties in terms of hardness and binding due to the addition of from about 1% to about 20% of divalent metal sulfates. Preferred levels of divalent metal sulfates are from about 1% to about 10%, most preferably from about 1% to about 5%. The divalent metal sulfates may be added at any step during the blending procedure.

The divalent metal sulfates can be hydrated or anhydrous. Preferred divalent metal sulfates used in the bar composition of the present invention include calcium sulfate, magnesium sulfate, and barium sulfate. Most preferably, the divalent metal sulfate is calcium sulfate. The types and amount of divalent metal sulfate can affect bar hardness. Preferably, the amount of any particular divalent metal sulfate (within the above-described percentage ranges) should be chosen so as to provide a bar hardness (measured with a force gauge) of about 52-70 lbs. after aging of the bar under normal atmospheric conditions.

A preferred test method measures bar hardness after three weeks of aging. Bars are aged for three weeks at 80°F/80 relative humidity (RH). To measure the bar hardness, a needle with a point angle of 43° attached to a force gauge (Control International, Lincolnwood, IL, USA) is forced onto the plane of the bar surface to a

depth of 5.8 mm. A preferred bar hardness reading of laundry bar compositions of the present invention having acceptable physical properties using this test method is about 55-70 lbs.

Adjunct Ingredients

Optional Surfactants

The detergent bars of the present invention can contain optional ingredients commonly used in detergent products. A typical listing of the classes and species of optional surfactants, (e.g. nonionic, zwitterionic and amphoteric surfactants) optional alkaline builders such as sodium carbonate trisodium phosphate sodium silicate, etc. and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992. Such optional surfactants, if present, can be included at levels up to a total of about 10%, preferably about 0.5-3%.

In addition, a hydrotrope, or mixture of hydrotropes, can be present in the laundry detergent bar. Preferred hydrotropes include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope is added to the linear alkyl benzene sulfonic acid prior to its neutralization. The hydrotrope, if present, will preferably be present at from about 0.5% to about 5% of the laundry detergent bar.

Builders

The laundry bars of the invention can contain from about 0% to about 60%, preferably from about 5% to about 25% detergent builder. These detergent builders can be, for example, water-soluble alkali-metal salts of phosphate, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. Preferred builders are a water-soluble alkali-metal salt of tripolyphosphate, and a mixture of tripolyphosphate and pyrophosphate. The builder can also be a non-phosphate detergent builder. Specific examples of non-phosphate, inorganic detergency builders include water-soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates, bicarbonates, and silicates are particularly useful herein. Specific preferred examples of builders include sodium tripolyphosphates (STPP) and tetra sodium pyrophosphates (TSPP), and mixtures thereof. Other specifically preferred examples of builders include zeolites and polycarboxylates.

Sodium carbonate is a particularly preferred ingredient in the subject invention compositions, since in addition to its use as a builder, it can also provide alkalinity to the composition for improved detergency, and also can serve as a neutralizing agent for

acidic components added in the composition processing. Sodium carbonate is particularly preferred as a neutralizing inorganic salt for an acid precursor of an anionic surfactant used in such compositions, such as the alkyl ether sulfuric acid and alkylbenzene sulfonic acid.

Co-polymers of acrylic acid and maleic acid are preferred in the subject compositions as auxiliary builders, since it has been observed that their use in combination with fabric softening clay and clay flocculating agents further stabilizes and improves the clay deposition and fabric softening performance.

Fabric Softening Clay

The fabric softening clay is preferably a smectite-type clay. The smectite-type clays can be described as expandable, three-layer clays; i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g. of clay. Preferably the clay particles are of a size that they can not be perceived tactilely, so as not to have a gritty feel on the treated fabric of the clothes. The fabric softening clay can be added to the bar to provide about 1% to about 50% by weight of the bar, more preferably from about 2% to about 20%, and most preferably about 3% to 14%.

While any of the smectite-type clays described herein are useful in the present invention, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite-type clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the instant compositions from the standpoint of product performance. On the other hand, certain smectite-type clays are sufficiently contaminated by other silicate minerals that their ion exchange capacities fall below the requisite range; such clays are of no use in the instant compositions.

Clay Flocculating Agent

It has been found that the use of a clay flocculating agent in a laundry bar containing softening clay provides surprisingly improved softening clay deposition onto the clothes and clothes softening performance, compared to that of laundry bars comprising softening clay alone. The polymeric clay flocculating agent is selected to provide improved deposition of the fabric softening clay. Typically such materials have a high molecular weight, greater than about 100,000. Examples of such materials can include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl

pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide) polymer. The amount of clay flocculating agent, if any, is about 0.2-2%, preferably about 0.5-1%.

Soil Suspending Agents

Soil suspending agents can be used. In the present invention, their use is balanced with the fabric softening clay/clay flocculating agent combination to provide optimum cleaning and fabric softening performance. Soil suspending agents can also include water-soluble salts of carboxymethylcellulose and carboxyhydroxymethylcellulose. A preferred soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan®, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof. If included, it can be at levels up to about 5%, preferably about 0.1-1%.

Other Optional Adjunct Ingredients

A particularly preferred optional component of the present invention is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of the softening clay and the clay flocculating agent.

The detergent chelant is preferably a phosphonate chelant, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1.

The detergent chelant can be included in the laundry bar at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, most preferably from about 0.5% to about 1.0%.

Another preferred additional component of the laundry bar is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 18 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol, if any, is present in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry bar as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

Another preferred optional component in the laundry bar is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitive dyes to prevent them from depositing on the fabrics, and decolorization DTI materials capable of decolorizing the fugitives dye by oxidation. An example of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyrridine N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also preferred for use herein. The amount of DTI included in the subject compositions, if any, is about 0.05-5%, preferably about 0.2-2%.

Another preferred optional component in the laundry bar is a secondary fabric softener component in addition to the softening clay. Such materials can be used, if any, at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include: amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R_7C00H, wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula R_8O-P(O)(OH)-OR_9 and HO-P(O)(OH)-OR_9, wherein

R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or Br^-, such as C_{12-13} alkyl trimethyl ammonium chloride.

Sodium sulfate is a well-known filler that is compatible with the compositions of this invention. It can be a by-product of the surfactant sulfation and sulfonation processes, or it can be added separately. Other filler materials include bentonite and talc.

Calcium carbonate (also known as Calcarb) is also a well known and often used filler component of laundry bars. Fillers include minerals, such as talc and hydrated magnesium silicate-containing minerals, where the silicate is mixed with other minerals, e.g., old mother rocks such as dolomite. Filler materials are typically used, if included, at levels up to 40%, preferably from about 5% to about 25%.

Optical brighteners are also preferred optional ingredients in laundry bars of the present invention. Preferred optical brighteners are diamino stilbene, distyrilbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis{[4-anilino-6-bis(2-hydoxyethyl) amino-1,3,5-trizin-2-yl]amino}stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition. If included, they are typically at levels up to about 0.5%.

Another optional component of the subject invention composition is a photobleach material, particularly phthalocyanine photobleaches which are described in U.S. Patent 4,033,718 issued July 5, 1977, incorporated herein by reference. Preferred photobleaches are metal phthalocyanine compounds, the metal preferably having a valance of +2 or +3; zinc and aluminum are preferred metals. Such photobleaches are available, for example, under the tradename TINOLUS or as zinc phthalocyanine sulfonate. The photobleach components, if included, are typically in the subject compositions at levels up to about 0.02%, preferably from about 0.001% to about 0.015%, more preferably from about 0.002% to about 0.01%.

Another useful optional component of the subject compositions are detergent enzymes. Particularly preferred are lipase, protease, amylase, and mixtures thereof. Enzymes, if included, are typically at levels up to about 5%, preferably about 0.5-3%.

Processing

The detergent laundry bars of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process, the raw materials are mixed in the blender. The divalent metal sulfates can be added at any point in the blender, but preferably, it is added after neutralization of the acid form of the detergent active. The alkyl benzene sulfonic acid is reacted with the mixture containing alkaline inorganic salts to complete neutralization, the amount of alkaline inorganic salt sufficient to completely neutralize the acid. Once the neutralization reaction is completed, other optional surfactants followed by any additional optional components such as chelants are added. It is most preferable to use as raw materials, such materials which contain little moisture. The mixing can take from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The bleach agent is added to the mixture and then mixed for an additional one to five minutes. It is usually added as one of the last ingredients, right before the perfume, if any, is added. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyer.

After milling or preliminary plodding, the product is then conveyed to a double vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

A preferred low moisture laundry bar composition is made by the following method: The raw materials are first mixed in a blender. Sodium carbonate and sodium tripolyphosphate is mixed for three minutes. A dose mixture of linear alkyl benzene sulfonic acid and sulfuric acid which have been pre-mixed for 1-1.5 minutes is then added to the blender, being completely neutralized by the sodium carbonate in the seat of the blender. (The amount of sodium carbonate is at least an amount sufficient to neutralize the acids.) The materials are mixed for an additional 1-2 minutes after dosing. Once the neutralization reaction is completed, divalent metal sulfates and optional surfactants are added, followed by any additional optional components such as chelants.

It is most preferable to use as raw materials, such materials which contain little moisture, so as not to exceed 3.5% total moisture in the finished product (exclusive of water of hydration of the divalent metal sulfate, if hydrated forms are used.). The mixing can take from one minute to one hour, with the usual mixing time being from about five to ten minutes. As one of the last ingredients, the bleach agent is added to the mixture and then mixed for an additional one to five minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyer.

After milling or preliminary plodding, the product is then conveyed to a double vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of the invention are set forth hereinafter by way of illustration and are not intended to be in any way limiting of the invention.

BAR EXAMPLES

The invention is illustrated by the following non-limiting examples. All parts and percentages herein are by weight unless otherwise stated.

Various bar compositions (Examples A through E) can be made using the methods described above.

	A	B	C
	(weight percent)		
Linear alkyl benzene sulfonate	12.5	7.5	8.5
Coco fatty alcohol sulfate	12.5	15.5	16.0
Soda Ash	14	14	15
Sulfuric acid	2.5	2.5	2.5
Sodium Tripolyphosphate	11.6	11.6	11.6
Calcium carbonate	39	37	27
Zeolite	1	0	1
Coco fatty alcohol	1	1	1
TiO_2	1	1	1
Perborate Monohydrate	2.25	4.5	10
Calcium Sulfate ($CaSO_4 1/2H_2O$)	5	0	2.5
Magnesium Sulfate	0	5	2.5

Fluorescent agents	0.2	0.2	0.2
Substituted methyl cellulose	0.5	0.5	0.5
Perfume	0.35	0.35	0.35
Moisture (final comp.)	3.0	1.3	3.0
Diethylenetriamine penta	0.9	0.9	0.9
Other conventional ingredients	Balance	Balance	Balance
	100	100	100

	D	E
	(weight percent)	
Linear alkyl benzene sulfonate	12.5	21
Coco fatty alcohol sulfate	12.5	0
Soda Ash	14	15
Sulfuric acid	2.5	2.5
Sodium Tripolyphosphate	11.6	12
Calcium carbonate	17	25
Sodium Sulfate	0	3
Magnesium Sulfate neptahydrate	0	3
$CaS0_402H_20$	5	0
Talc	0	10
Coco fatty alcohol	1	1
TiO_2	1	1
Perborate Monohydrate	15	5
Protease enzyme	0.0	0.08
Fluorescent agents	0.2	0.2
Substituted methyl cellulose	0.5	1.4
Perfume	0.35	0.35
Moisture (final comp.)	2.8	2.3
Other conventional ingredients	Balance	Balance
	100	100

WHAT IS CLAIMED IS:

1. A laundry detergent bar composition comprising:
   (a) from about 0.5% to about 60% synthetic anionic detergent surfactant, wherein at least 30% of said synthetic anionic detergent surfactant is linear alkyl benzene sulfonate;
   (b) from about 0.10% to about 60% bleach agent;
   (c) no more than about 3.5% moisture in the finished bar composition; and
   (d) from about 1% to about 20% divalent metal sulfate.

2. A bar composition as claimed in Claim 1, wherein at least 50% of said synthetic anionic detergent surfactant is linear alkyl benzene sulfonate.

3. A bar composition as claimed in Claim 2, comprising from about 1% to about 10% divalent metal sulfate.

4. A bar composition as claimed in Claim 3, wherein said divalent metal sulfate is selected from the group consisting of calcium sulfate, magnesium sulfate, barium sulfate, and mixtures thereof.

5. A bar composition as claimed in Claim 3, comprising from about 1% to about 50% bleach agent, wherein said bleach agent is a peroxygen bleach.

6. A laundry detergent bar composition comprising:
   (a) from about 10% to about 30% synthetic anionic detergent surfactant, wherein at least 50% of said synthetic anionic detergent surfactant is linear alkyl benzene sulfonate;
   (b) from about 1% to about 20% bleach agent;
   (c) no more than about 3.5% moisture in the finished bar composition; and
   (d) from about 1% to about 5% divalent metal sulfate.

7. A bar composition as claimed in Claim 6, further comprising from about 5% to about 25% builder.

8. A bar composition as claimed in Claim 6, wherein said bleach agent is a peroxygen bleach.

9. A bar composition as claimed in Claim 6, wherein said divalent metal sulfate is selected from the group consisting of calcium sulfate, magnesium sulfate, barium sulfate, and mixtures thereof.

10. A bar composition as claimed in claim 9, wherein said bleach agent is sodium perborate.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/17373

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D3/39 C11D1/14 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 28102 A (PROCTER & GAMBLE) 8 December 1994 see claims 6-10; examples V,XIII ---	1-10
A	WO 95 27038 A (PROCTER & GAMBLE) 12 October 1995 see page 16, line 19 - line 32; claims 1-11; examples 2,4,7-9 ---	1-10
A	DE 43 19 577 A (HENKEL KGAA) 15 December 1994 see page 4, line 61; claims 1-5; examples 1-3 ---	1-10
A	BE 775 446 A (CONTINENTAL OIL CO) 16 March 1972 see page 9, line 1 - line 15; claims 1-5; example 1 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 July 1997	25.07.97

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Interr ıal Application No
PCT/US 96/17373

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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